Pacific Northwest
NATIONAL LABORATORY

Reversible ketone hydrogenation and dehydrogenation for aqueous organic redox flow batteries

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Science, **2021**, *372*, 836.

DOE-OE Peer Review 2021
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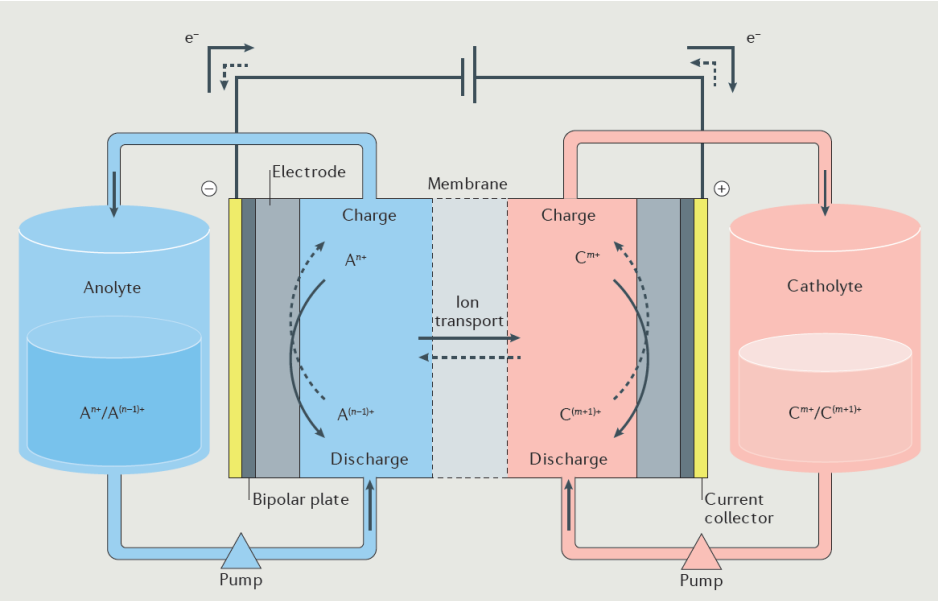
U.S. DEPARTMENT OF ENERGY BATTELLE

Redox Flow Batteries (RFB)



Nat. Rev. Mater **2016**, *2*, 16080.

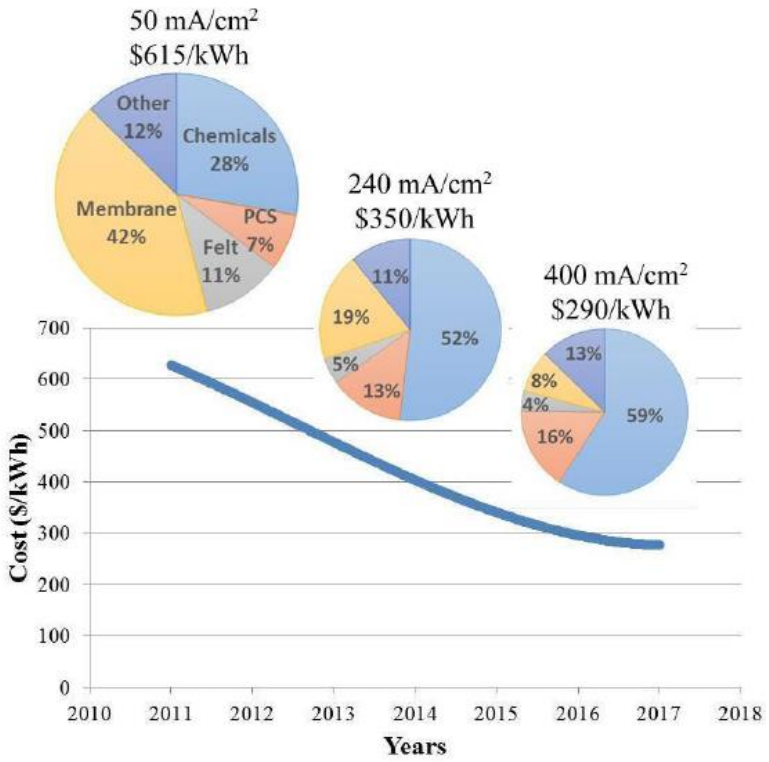
Technology suitable for

Long Duration Energy Storage

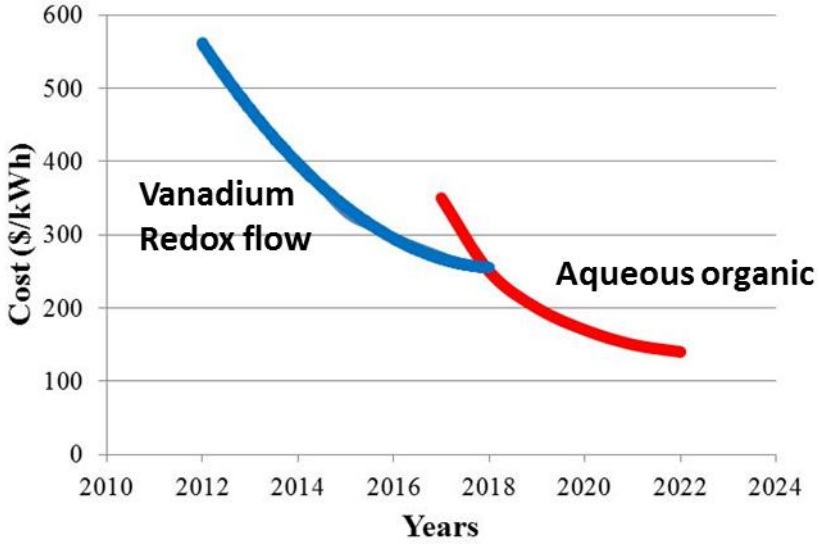
- **Modular design**
  - Decoupled energy storage and power generation
  - Versatile application
- **High safety**
  - Spatial separation of reactive materials
  - water based electrolyte
  - Easy thermal management
  - Battery health monitoring
- **Easy material recycling after service life**
  - Consumption vs. Investment

From Vanadium *evolving into* Organics

- **Vanadium Redox Flow Battery (VRB)**
  - Current state-of-the-art, highly studied
  - High material capital cost

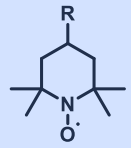
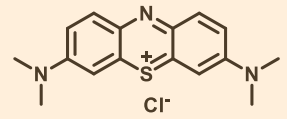
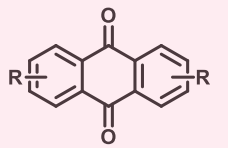
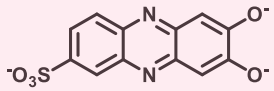
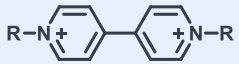
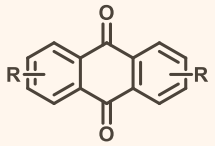


- **Benefits of Organics**
  - Potentially lower material cost on large scale
  - Tunability of material and supporting electrolyte
  - Candidates with 2e$^-$ redox events



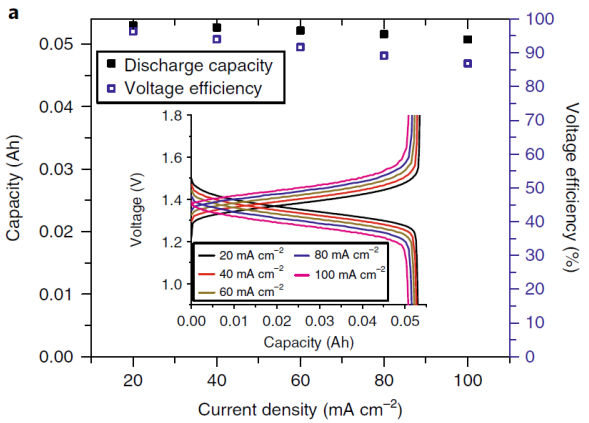
New materials development to
- ***drive down cost***
- ***improve performance***

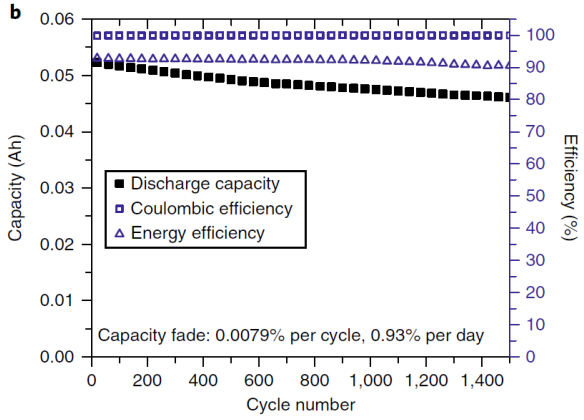
Common examples of active material

	Alkaline condition	Neutral condition	Acidic condition
Positive electrolyte	$K_3Fe(CN)_6$		
Negative electrolyte	 		

Limited library

Top Challenge Material Stability





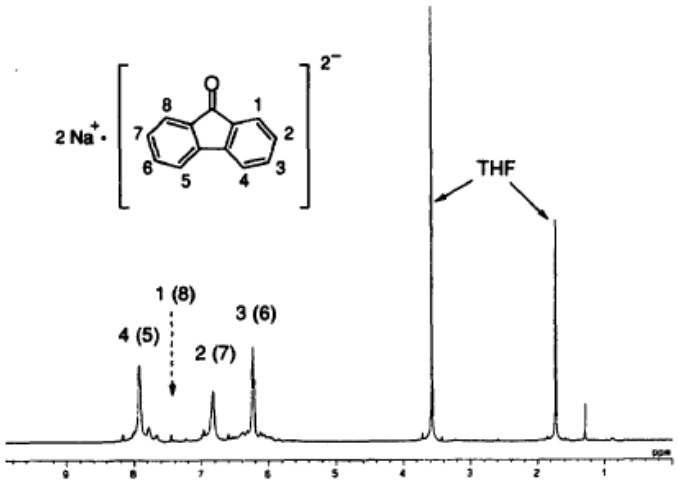
- ✓ **2e redox event**
- ✓ **High energy density**
- ✓ **Fast kinetics**

Improve cycling stability

Nat. Energy **2018**, *3*, 508-514.

Fluorenone (FL) core structure

Highly stable FL ring structure Even at charged state

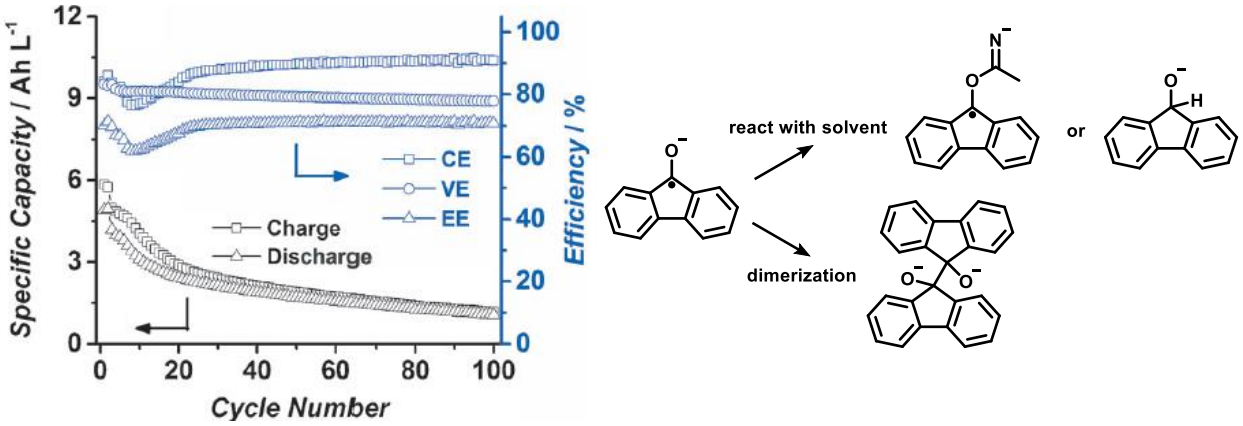


FL dianion in THF-*d8* reflux at 66°C for half year

Tetrahedron Letters **1999**, *40*, 7347-7350.

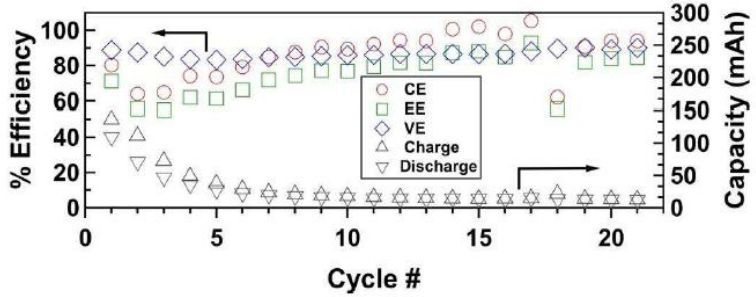
FL/FL radical anion: 1e redox chemistry in RFB

Nonaqueous system



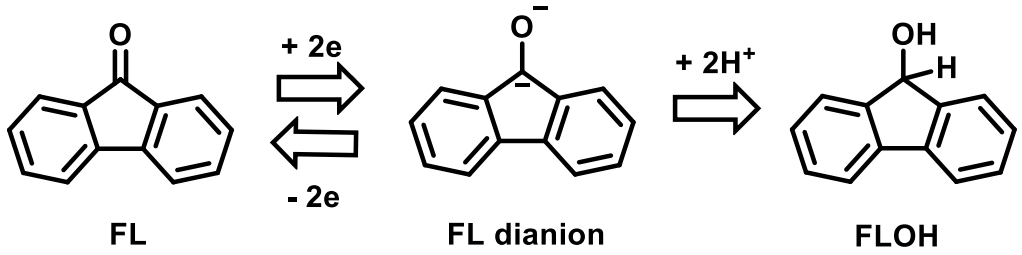
Angew. Chem. Int. Ed. **2015,** *54*, 8684.

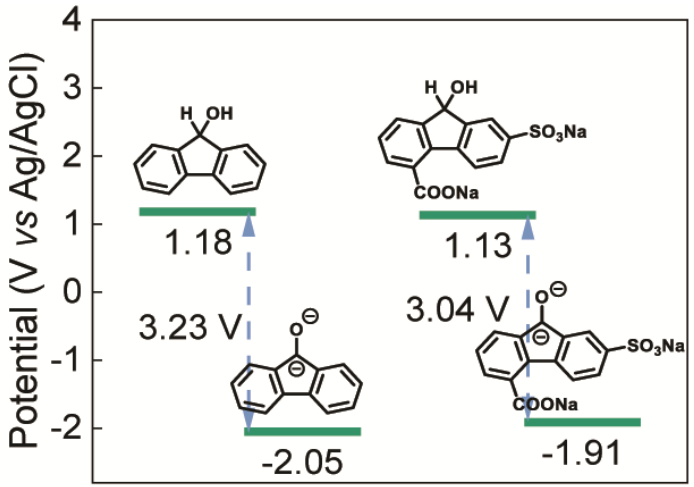
Aqueous system



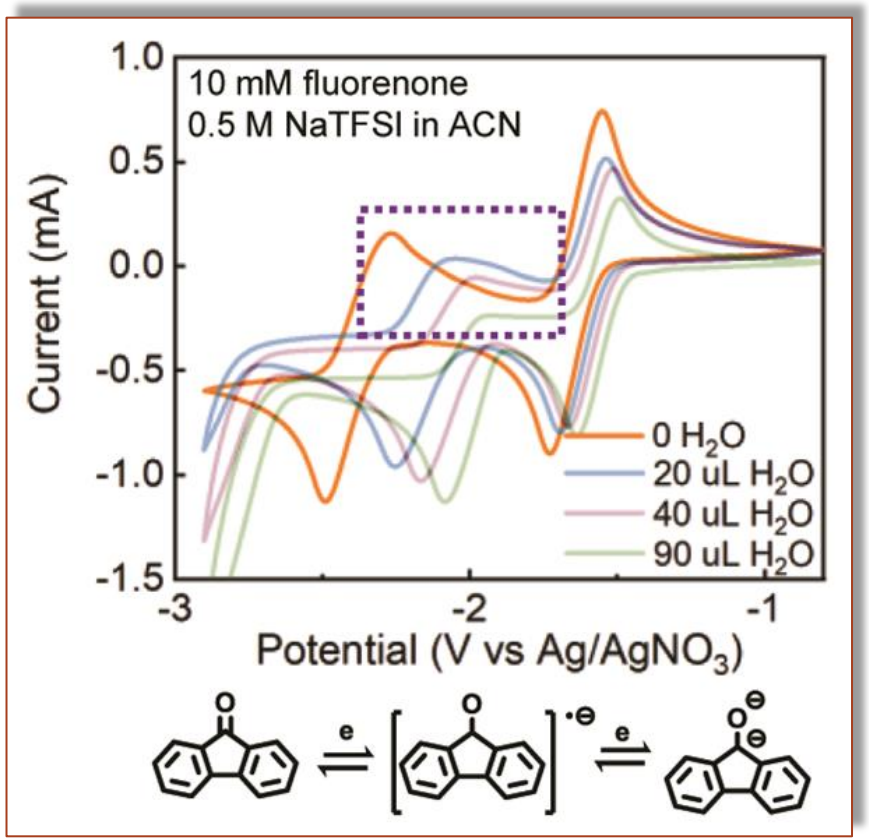
ECS Trans. **2019**, *89*, 49-59.

Ketone hydrogenation





DFT calculation of oxidation potential on dianion and alcohol



- Electrochemical irreversible
- Protonation leads to loss of reversibility

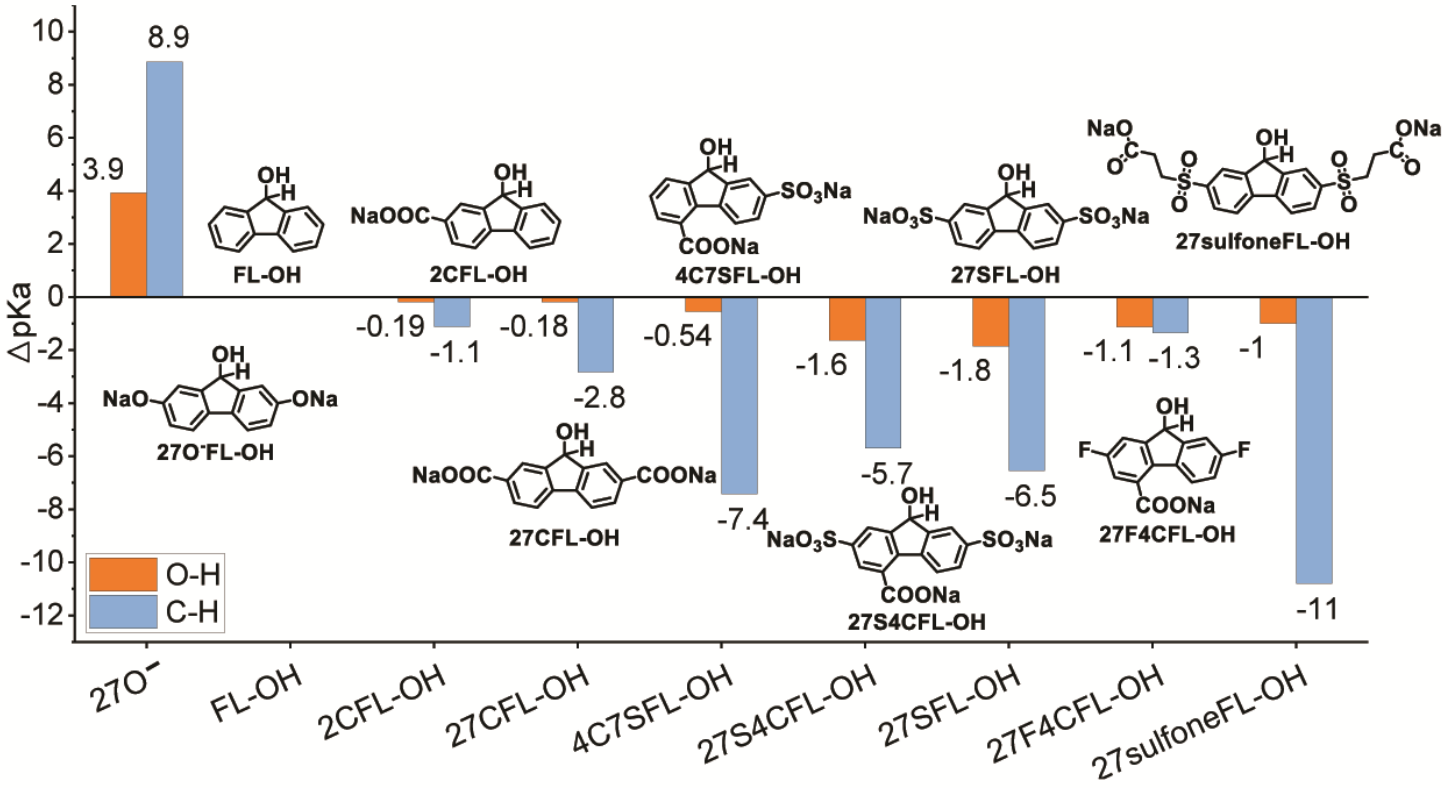
Design strategy

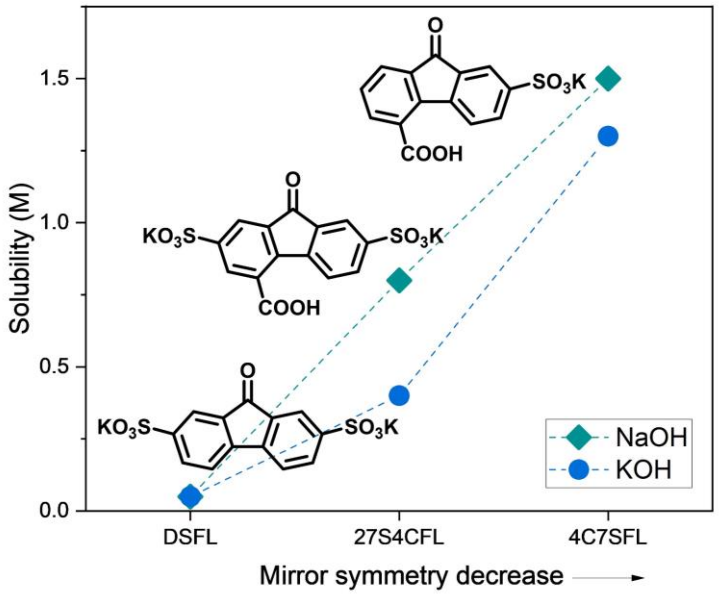
❖ Reversibility

- ➢ Electron Withdrawing Group (EWG) for acidic C-H
- ➢ Re-generate anionic species

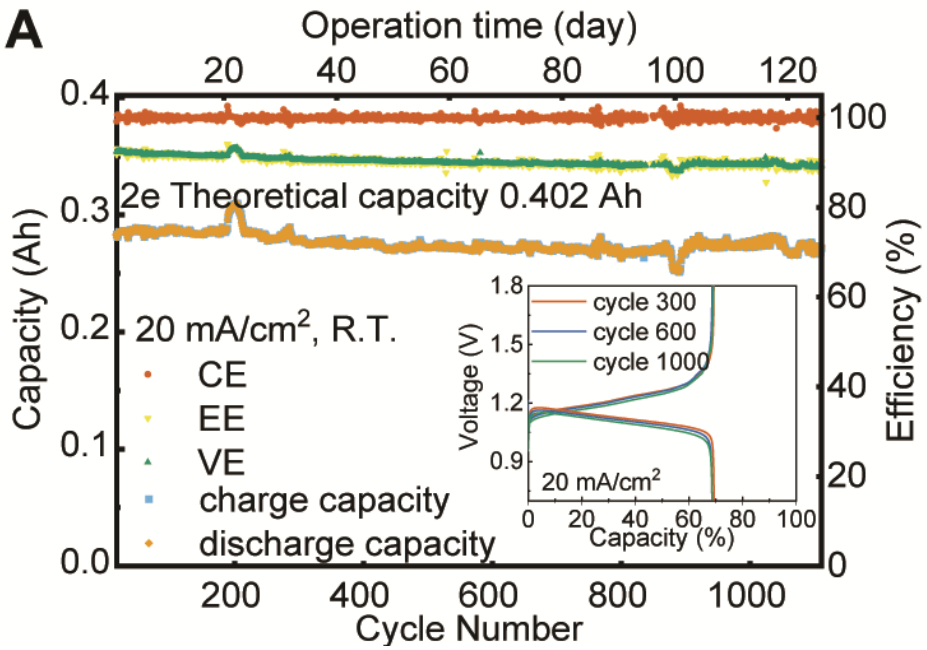
❖ Solubility

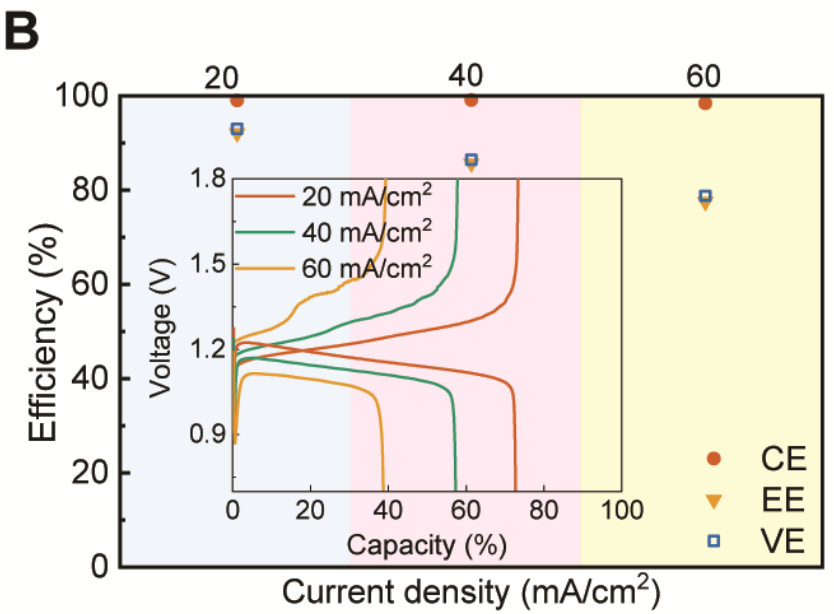
- ➢ Carnelley's rule
- ➢ Asymmetric molecule





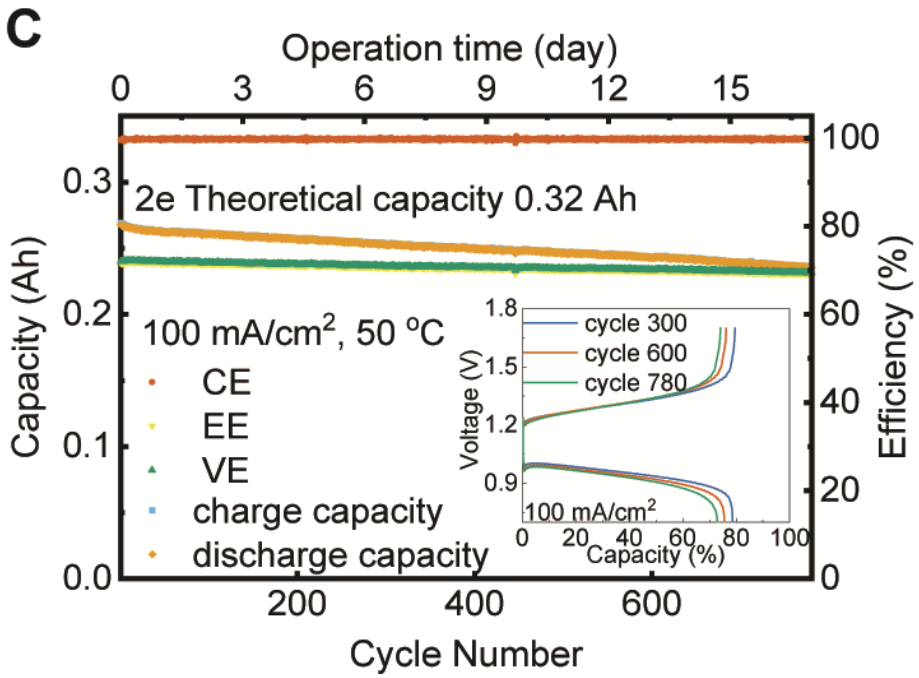
Battery performance at room temperature

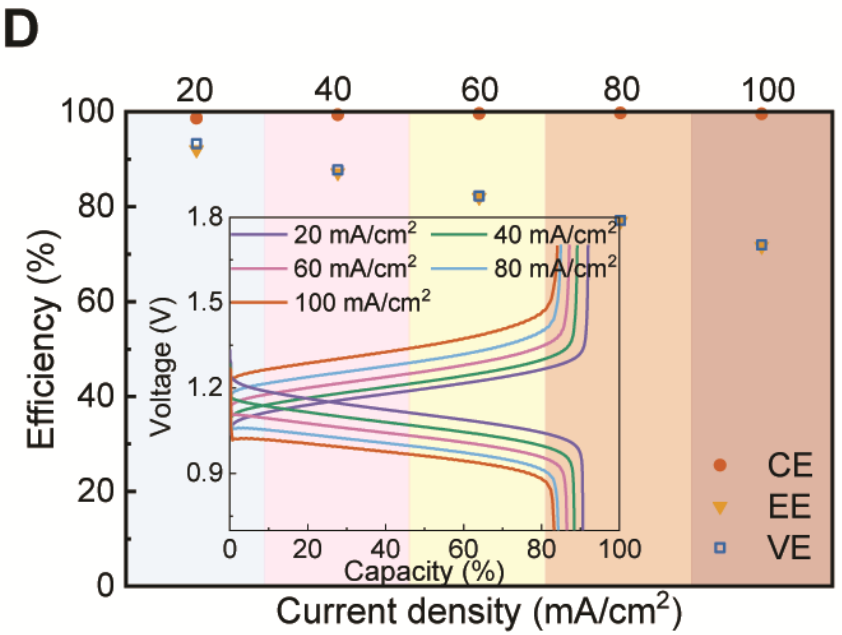




- 4-month continuous cycling at constant current
- 0.02%/day observed battery capacity decay (minor de-sulfonation)
- 90% Energy efficiency (EE)
- Reasonable rate on demonstrated benchtop scale

Battery performance at elevated temperature

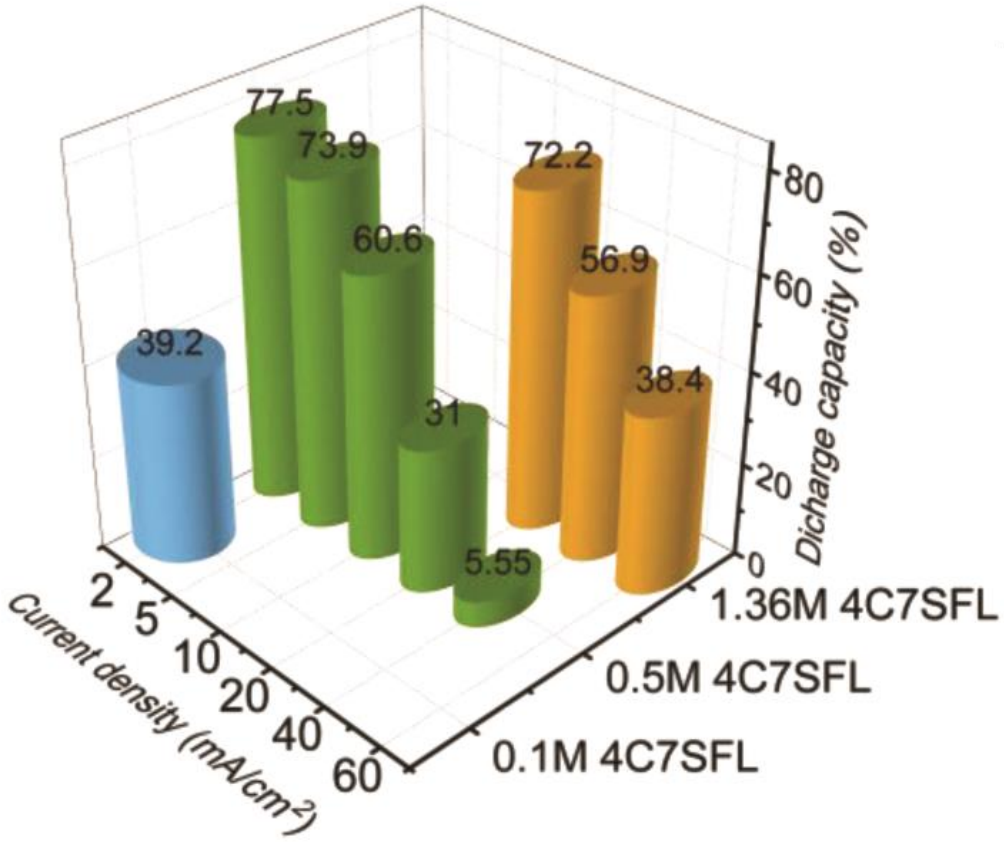




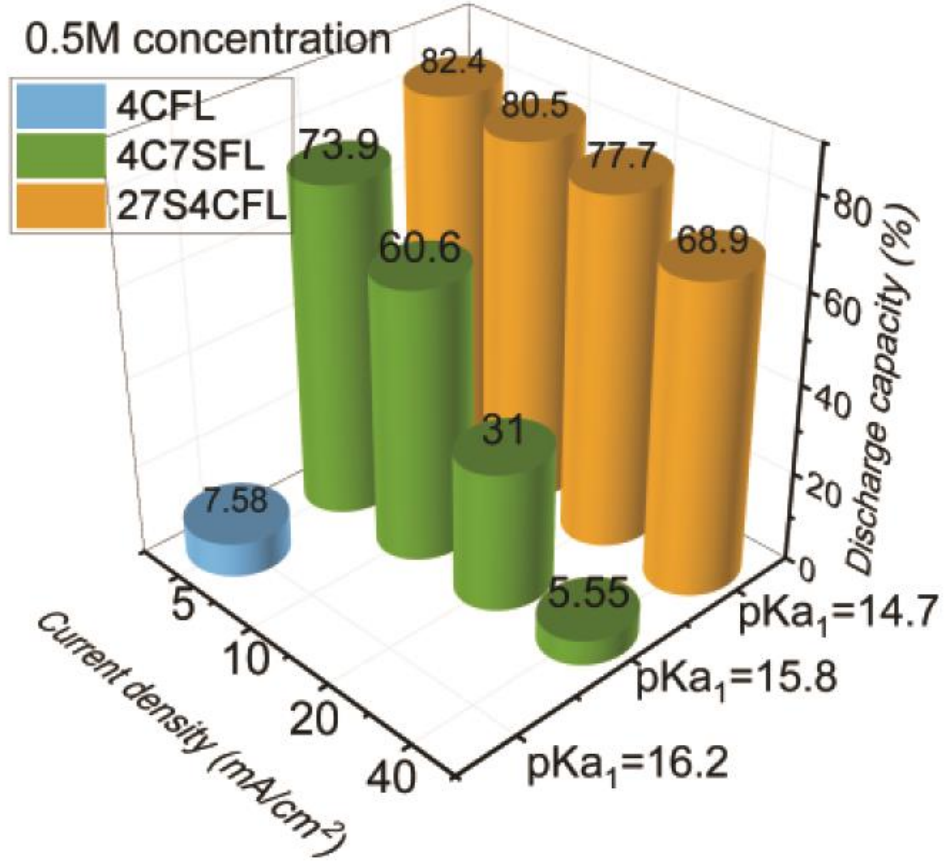
- Stable cycling at elevated temperature (50 °C) and ambient environment
- 70% Energy efficiency (EE) at 100mA/cm2 on benchtop cell (10cm2 cell)
- Faster decay observed due to crossover and other issues

Observe unconventional cycling behavior

Concentration dependent discharge reversibility

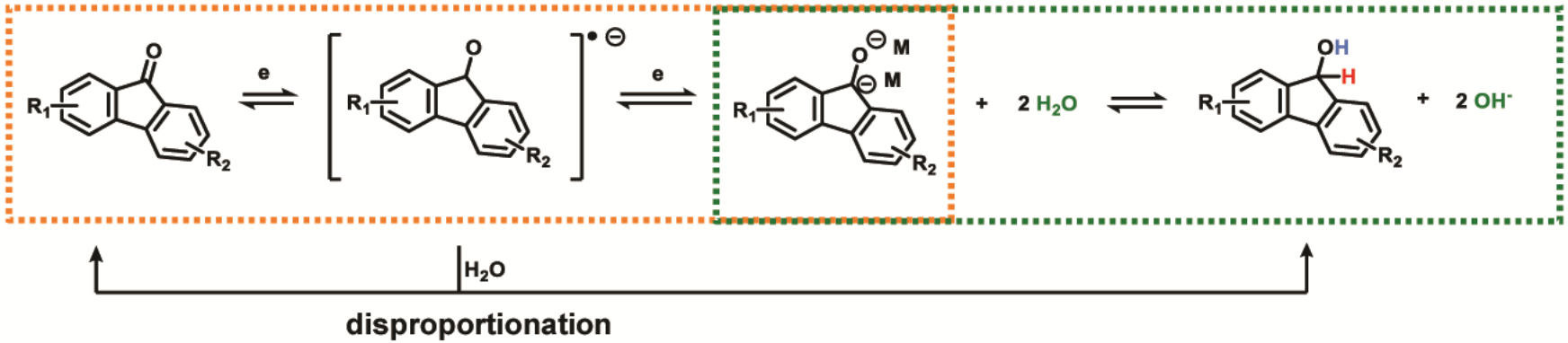


pKa dependent discharge reversibility



Validate EWGs needed to support discharge

Apply unconventional redox mechanism



- electrochemical process coupled with chemical reaction
  - ❖ First reported redox mechanism that couple chemical reaction for RFB
- Deprotonation of the C-H is vital to initiate reversible discharge
  - ❖ First reported strategy that activate redox in-active material

Summary

Summary

- High energy density FL based anolyte material developed with **2e** redox chemistry
- High stability FL based flow battery demonstrated for continuous **4-month** cycling
- New redox mechanism discovered for flow battery; potential library expanded

Recognition from the field

"These FL anolytes not only display exceptional energy storage performance but also exhibit an unprecedented two-electron storage mechanism."

T. Leo Liu, etc. *Science*, **2021**, *372*, 788.

"The study by Feng et al. is significant in this context because it not only introduces an entirely new class of organic molecule as a candidate in aqueous RFBs, but also offers a strategy for activating redox activity in a molecule that is natively redox-inactive."

David G. Kwabi, *Joule*, **2021**, *5*, 1636-1638.

Future Direction

- Achieve higher power density /current density

Acknowledgements

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Thank You For Your Attention

Questions?

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